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A review of intercalation composite phase change material: Preparation, structure and properties

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ABSTRACT

This paper reviews preparation, structure and properties of the intercalation composite phase change material (PCM). The layered structure of clay and graphite is utilized to prepare the intercalation composite PCM. It is concluded that the preparation methods include liquid phase intercalation and melting intercalation. The thermal conductivity and flame retardancy of organic PCM are improved by intercalating organic PCM into montmorillonite (MMT) or graphite. The phase change properties of the intercalation composite PCM can be measured by differential scanning calorimetry (DSC) and T-history method.

Contents

1. Introduction

After the oil crisis in 1970s, the applications of energy storage technique in the energy conservation field have gained attached great importance. Many kinds of energy are intermittent, for example, solar energy. Therefore, energy storage plays an important role in storing the releasing energy. With the improvement of people's living standards, the requirement for the indoor comfortability becomes higher and higher and the energy consumption due air conditioning increased sharply. As a result, some problems are caused, such as excessive energy consumption, increment of emission of carbon dioxide and environment pollution and severe deficiency of electric power supply in the peak load. Nowadays many cities of china are carrying out the policy of different power

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fare during different period to alleviate burdens of load peaks. The frequency of using air conditioning will be reduced if PCM is used to store solar energy in the daytime and release solar energy at night in winter, or oppositely in summer for cool load [1–8].

The thermal storage includes sensible heat storage and latent heat storage (phase change). The sensible heat storage is carried out by utilizing the natural heat storing capacity of materials. The advantage of such storage is the simplicity. The disadvantage however is that rather large volumes are required and that the energy is released at varying temperature. Phase change energy storage is carried out by storing and releasing latent heat during the phase change (solid–liquid, solid–solid, gas–liquid). Advantages of PCM are high storage density and constant temperature during phase change. Therefore, PCM is lately gaining an increasing interest [9–14].

This paper reviews the studies conducted on preparation, structure and properties of the intercalation composite PCM. So, Section 2 deals with classification and characteristics of PCM. Section 3 deals with preparation method of the intercalation composite PCM. Structure characterization of intercalation composite PCM is developed in Section 4. Section 5 is dedicated to properties of the intercalation composite PCM.

2. Classification and characteristics of PCM

2.1. Classification by composition

PCMs are classified as inorganic PCM, organic PCM and composite PCM by composition. Inorganic PCMs include crystallographic hydrous salts, molten salts, metal and alloy. Organic PCMs mainly include paraffin and fatty acid. Detailed information about PCM can be found in papers [15–18].

Commercial paraffin has a lot of advantages, such as low price, suitable density of energy storage (200 kJ/kg), wide melting range, chemical inertness, and having no corrosivity and supercooling. However, it has low thermal conductivity (about 0.2 W/m °C) which restricts its application.

Fatty acid has similar properties as paraffin. Feldman and Shapiro [19] analyzed the thermal properties of fatty acids and their mixture. The results indicate that their melting point is 30–65 °C and their latent heat capacity is 153–182 kJ/kg. Hasan [20] investigated experimentally the phase transition time, temperature range of phase transition, transfer of solid–liquid interface and heat transfer rate of palmitic acid. Dimaano [21] studied the mixture of decanoic acid and lauric acid, whose melting point is 14 °C and the latent heat capacity is 113–133 kJ/kg.

Hydrous salts are widely applied as they show higher bulk heat storage density and thermal conductivity than those of paraffin. $Na_2SO_4 \cdot 6H_2O$, one of the cheapest PCMs, was studied from 1952. Its melting point is 32.4 °C and the latent heat capacity is 254 kJ/kg [22]. Nevertheless, it has the phenomenon of phase separation and supercooling.

The thermal properties of organic and inorganic PCMs are compared in Table 1. Table 1 shows that PCM has higher latent heat density than sensible heat storage materials and inorganic PCM has higher latent heat density than organic PCM.

2.2. Classification by the phase

PCMs can be classified as solid–solid PCM, solid–liquid PCM, solid–gas PCM and liquid–gas PCM. Solid–liquid PCMs include inorganic PCM, such as crystallographic hydrous salts, molten salts, metal, alloy, and organic PCM, such as higher aliphatic hydrocarbon, fatty acid, and high molecular weight polymer. The advantage of the solid–liquid PCM is low cost and the disadvantage is having the phenomenon of phase separation and supercooling which lead to easy leakage, environment pollution and high corrosivity. The solid–solid PCMs include crosslink high density polyethylene, layered calcium titanium and polyatomic alcohol [24]. Their advantages are little volume variety, little subcooling degree, no corrosion, high heat efficiency and long service life. However, they are expensive and have poor thermal conductivity. In addition, they turn into volatile plastic crystal over the phase change temperature. The thermal properties of some PCMs are listed in Table 2 [25].

3. Preparation of intercalation composite PCM

Layered materials include organic silicate, phosphate, layered double hydroxide and graphite. The basal spacing is around a few nanometers and there is removable ion or neutral molecule in the interlayer. The interaction force, like van der Waals force and electrostatic force is weak. The layered material has two special properties decided by their structure. One is interchangeability of ions between layers. The other is that the production after exchanging has high stability and the layered structure is not destroyed [26–29]. Although the layered material has no special properties itself, the function of the composite can be improved by introducing some guest molecules.

There are mainly two kinds of layered composite PCM mentioned in the present papers. One is the clay-based composite PCM and the other is the graphite-based composite PCM. They have similar preparation method.

3.1. The clay-based composite PCM

In the past 20 years, much interest has been focused on the behavior and properties of the surfactant/clay hybrids. These hybrids are synthesized by intercalating surfactant molecules into the phyllosilicate interlayer. The fundamental structure of layered silicates is silicon–oxygen tetrahedron and aluminum–oxygen octahedron. They may form 1:1 type or 2:1 type layered clay. Among these phyllosilicates, montmorillonite (MMT) has been extensively investigated as a host due to its excellent properties, such as cationic exchangeability, swelling behavior, sorption properties, and large surface area. MMT has a kind of sandwiched structure and the clay layer was negatively charged, which is counterbalanced by exchangeable cations in the galleries between layers. MMT belongs to 2:1 type layered clay and its structure is

Table 1
Comparison of heat storage ability of different materials [23].

Property	Rock	Water	Organic PCM	Inorganic PCM
Density (kg/m^3)	2240	1000	800	1600
Specific heat (kJ/kg)	1.0	4.2	2.0	2.0
Latent heat (kJ/kg)	–	–	190	230
Latent heat (kJ/m^3)	–	–	152	368
Storage mass for 10^6 J (kg)	67,000	16,000	5300	4350
Storage volume for 10^6 J (m^3)	30	16	6.6	2.7
Relative storage mass	15	4	1.25	1.0
Relative storage volume	11	6	2.5	1.0

Table 2
Thermal properties of PCMs [25].

Compound	Melting temp. (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m^3)
Inorganics				
$MgCl_2 \cdot 6H_2O$	117	168.6	0.570 (liquid, 120 °C) 0.694 (solid, 90 °C)	1450 (liquid, 120 °C)1569 (solid, 20 °C)
$Mg(NO_3)_2 \cdot 6H_2O$	89	162.8	0.490 (liquid, 95 °C) 0.611 (solid, 37 °C)	1550 (liquid, 94 °C) 1636 (solid, 25 °C)
$Ba(OH)_2 \cdot 8H_2O$	48	265.7	0.653 (liquid, 85.7 °C) 1.225 (solid, 23 °C)	1937 (liquid, 81 °C) 2070 (solid, 24 °C)
$CaCl_2 \cdot 6H_2O$	29	190.8	0.540 (liquid, 38.7 °C)0.1088 (solid, 23 °C)	1562 (liquid, 32 °C) 1802 (solid, 24 °C)
Organics				
Paraffin wax	64	173.6	0.167 (liquid, 63.5 °C)0.346 (solid, 33.6 °C)	790 (liquid, 65 °C) 916 (solid, 24 °C)
Polyglycol E600	22	127.2	0.189 (liquid, 38.6 °C) –	1126 (liquid, 25 °C) 1232 (solid, 4 °C)
Fatty acids				
Palmitic acid	64	185.4	0.132 (liquid, 68.4 °C) –	850 (liquid, 65 °C) 989 (solid, 24 °C)
Capric acid	32	152.7	0.153 (liquid, 38.5 °C) –	878 (liquid, 45 °C) 1004 (solid, 24 °C)
Caprylic acid	16	148.5	0.149 (liquid, 38.6 °C) –	901 (liquid, 30 °C) 981 (solid, 13 °C)

shown in Fig. 1. Utilizing the exchangeability, intercalation and swelling property of MMT, MMT intercalation composite PCM is prepared by inserting organic PCM into interlayer of MMT [30,31].

3.1.1. Organic modification of the layered clay

The incompatibility between clay and organic PCM and small basal spacing of the layered clay make it non-beneficial for organic material to intercalate into the interlayer. So organic modification is needed to improve the relation between surface atoms of clay and organic PCM for obtaining the clay composite with good intercalation and dissociation effect.

Cai et al. modified MMT with alkyl-amines [32]. Org-MMT was prepared by treating Na-MMT with hexadecyltrimethyl ammonium bromide by Fang and Zhang [33]. Xiao et al. used different alkyl-amines (ammoniums) such as n-butylamine, n-octylamine, dodecylamine, hexadecylamine, octadecylamine and hexadecyltrimethyl ammonium bromide to investigate the influence of carbon numbers of the alkyl-amines (ammoniums) on the intergallery distance of the organically modified clay. Moreover, they studied the effects of organically modifying time on the intergallery distance of the organic MMT (OMMT) [34].

In the process of organic modification, alkyl-amine ions immerge into layers of MMT by ion exchange reaction. The surface of layers is covered with long alkyl carbon chain and changed to lipophilicity from hydrophilicity. This increases the compatibility of OMMT and organics. Thus, organics can be intercalated into interlayer of MMT [35]. Ideal model of organically modified clay is shown in Fig. 2 [36].

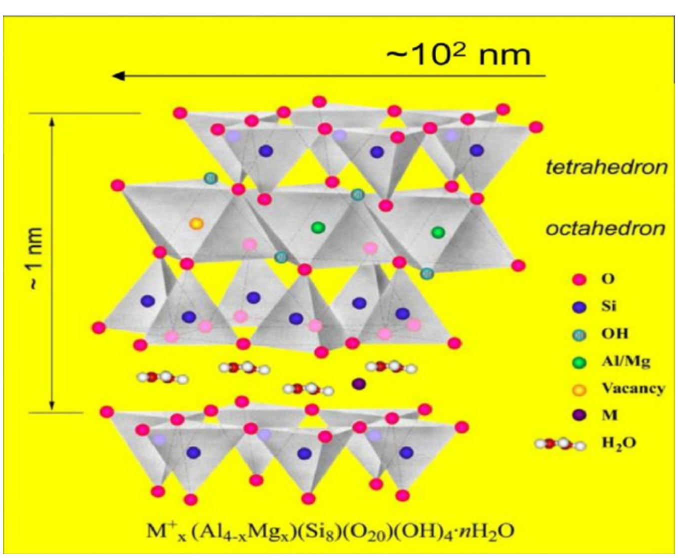


Fig. 1. Structure diagram of montmorillonite.
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Long carbon link alkyl-amines can also be used for organic modification besides alkyl quaternary ammonium salts with long carbon link. Zhu et al. synthesized rigid aromatic amine. The MMT modified by the rigid aromatic amine presented greater basal spacing and better thermal stability than that modified by the aliphatic amine [37]. The choice of intercalating agent of MMT should confirm the following conditions [38]:

1. The basal spacing between silicate crystals (0 0 1) is remarkable.
2. There is strong physical and chemical reaction between intercalating agent molecules and organics to make intercalation easier.
3. Cheap and easy to get.
4. Biodegradable and environmentally friendly.

Three following aims are obtained by organic modification of MMT:

1. Hydrate inorganic cations in interlayer of MMT are exchanged.
2. The basal spacing of MMT is enlarged.
3. The binding force between MMT and organics is improved.

3.1.2. Preparation of clay-based intercalation composite PCM

The following two kinds of intercalation method are reported in present studies:

1. *Liquid intercalation method*. The organic PCM is intercalated into interlayer of inorganic in solution by virtue of solvent. Zhou and Zhou prepared paraffin/MMT nano-composite phase change materials using liquid intercalation method. MMT is put into

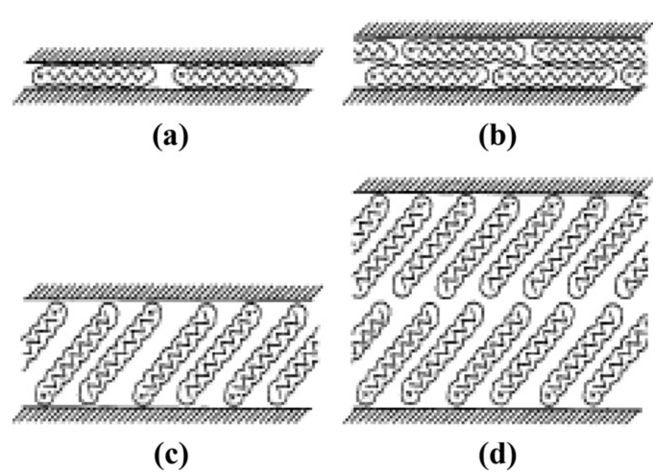


Fig. 2. Alkyl chain aggregation in mica-type silicates: (a) lateral monolayer; (b) lateral bilayer; (c) paraffin-type monolayer; (d) paraffin-type bilayer [36].

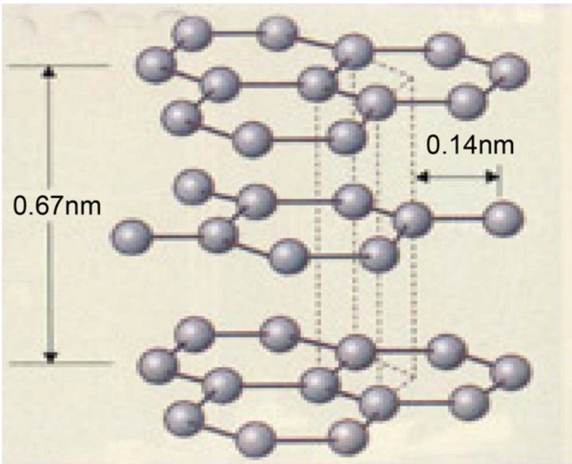


Fig. 3. Structure diagram of graphite.

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water and stirred and the gel of MMT is formed. Then the molten paraffin is added into the gel of MMT and stirred at high speed. The paraffin/MMT nano-composite PCM with "oil-in-water" structure is formed [39]. This method needs suitable solvent to dissolve organic PCM and disperse the layered materials. Significant quantity of solvent is difficult to volatile, which will cause adverse effects to the environment.

2. *Melting intercalation method*. The organic PCM is heated above the melting point and intercalated into the interlayer of the layered materials by mixing, stirring and ultrasonic method. Fang and Zhang prepared MMT-based composite PCM using melting intercalation method [40]. They mixed PCM and OMMT uniformly and then put them in the drying oven at 50 °C for 20 min. The sample is ground after being cooled and the composite PCM is obtained. Chen et al. prepared lauric acid/organophilic montmorillonite shape-stabilized PCM by using a melting intercalation technique [41]. Li and He also prepared OMMT and organic phase change energy storing material using melting intercalation method [42]. This method is simple and organic solvent is not needed in the preparation process.

3.2. Preparation of graphite-based intercalation composite PCM

Graphite is hexagonal crystal and has layered structure. The weak van der Waals force connects the layers and the basal spacing is 0.3345 nm. Owing to the weak binding force between carbon layers, external atom, molecules and ions may intercalate into the interlayer without destroying the hexagonal reticulate structure in a single carbon layer. The crystal structure of graphite is presented in Fig. 3.

The basal spacing of graphite is small and the surface of the layer has neither hydrophilicity nor hydrophobicity. Therefore, it is difficult for organic molecules to intercalate into the layers of graphite. This restricts the application of graphite in thermal storage field. The basal spacing can be enlarged or exfoliated by acid oxidation and explanation. The natural graphite flakes are added into sulfuric acid and stirred for 60 min at 50 °C. Then the reaction products are washed until the liquid is neutral and then are dried. The expandable graphite is obtained. The expanded graphite is prepared by heating the expandable graphite for 10–30 s at 900–1000 °C [43,44]. The exfoliated graphite is used to prepare the intercalation composite PCM by the liquid phase intercalation and melting intercalation. The two preparation methods are similar with the preparation method of clay-based intercalation composite PCM [45–47].

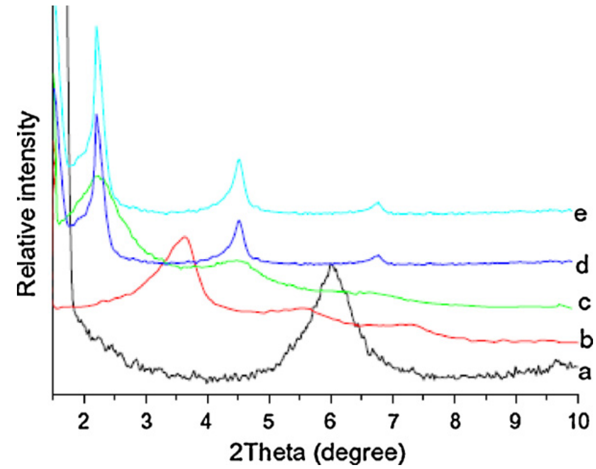


Fig. 4. XRD patterns of (a) MMT; (b) OMT; (c) HDPE–EVA/OMT (5 wt%) nanocomposites; (d) PCM3 and (e) PCM4 [48].

4. Structure characterization of intercalation composite PCM

4.1. X-ray diffraction (XRD) analysis

X-ray diffraction is applied to characterize the phase composition of materials because of its simplicity in operation and efficiency. XRD analysis can prove directly whether organics have been introduced into interlayer of layered materials or not. A series of diffraction peaks appear in the XRD diffraction images for well crystallized layered materials. The attribution of the diffraction peaks can be calculated by the Bragg formulation and the (0 0 1) diffraction peak is obtained. The basal spacing is increased when organics are introduced into interlayer of layered materials. This represents the movement of the first-order diffraction peak towards small angle in the XRD diffraction images.

Fig. 4 presents the XRD patterns of MMT, OMT, HDPE–EVA/OMT (5 wt%) nanocomposites, PCM3 and PCM4 [50]. The peaks correspond to the (0 0 1) plane reflection of the clays. The average basal spacing of OMT increases from 1.5 nm of original MMT to 2.4 nm. The increased spacing suggests the chains of hexadecyltrimethyl ammonium bromide (C16) intercalate into the gallery of MMT and expand it. The intercalated morphology of HDPE–EVA/OMT (5 wt%) MMT (Fig. 4c) is proved by the interlayer spacing, which is derived from the *d*0 0 1 peak of MMT and is increased from 2.4 nm for OMT (Fig. 4b) to 3.8 nm. The 1.4 nm galley height increase indicates the intercalated nanostructure has been formed. The basal spacing of PCM3 (Fig. 4d) and PCM4 (Fig. 4e) is 3.9 nm, which has a 1.5 nm gallery height increase compared with OMT.

Fig. 5 shows the XRD patterns of MMT/PCM intercalation composite PCM [39]. The XRD pattern of MMT/PCM composite PCM indicates (0 0 1) diffraction peak which represents the basal spacing of MMT weakens remarkably. This illustrates that most MMT has been dissociated under the effect of water and do not combine again because of the barrier of PCM. Layers of MMT overlap with each other and cavities are formed to contain PCM.

4.2. Scanning electron microscope (SEM) analysis

The thickness of layer and the change of the basal spacing can be observed directly using SEM. Zhang and Fang [49] observed the microstructure of expanded graphite and paraffin/expanded graphite composite PCM. The results are shown in Fig. 6.

Fig. 6 indicates that expanded graphite has a worm-like appearance of its particles. After the paraffin had been absorbed into the

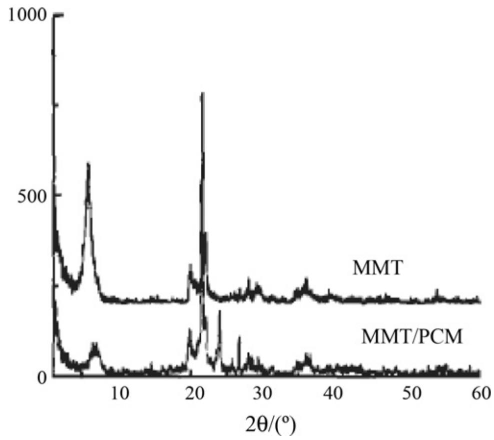


Fig. 5. XRD patterns of MMT/PCM composite PCM [39].

pores of the expanded graphite, the expanded graphite remained in the worm-like structure, and the absorbed paraffin exhibited a uniform distribution in the paraffin/expanded graphite composite PCM owing to the capillary force and the surface tension force of the porous expanded graphite.

Kim et al. [50], Fang et al. [51], Xia et al. [52] also characterized the micro-structure of intercalation composite PCM using SEM. Mills et al. [45] observed the surface structure of graphite and graphite/paraffin composite PCM. The layers and interlayer structure of graphite, the intercalating state of paraffin in graphite are observed. It is clear that the paraffin wax is primarily found as a thin layer on the graphite surfaces.

4.3. Fourier transformation infrared ray (FTIR) analysis

FTIR can characterize the combining situation between organics and layered materials.

The structure changes of intercalation composite PCM are judged by the changes of FTIR peaks. This is attributed to

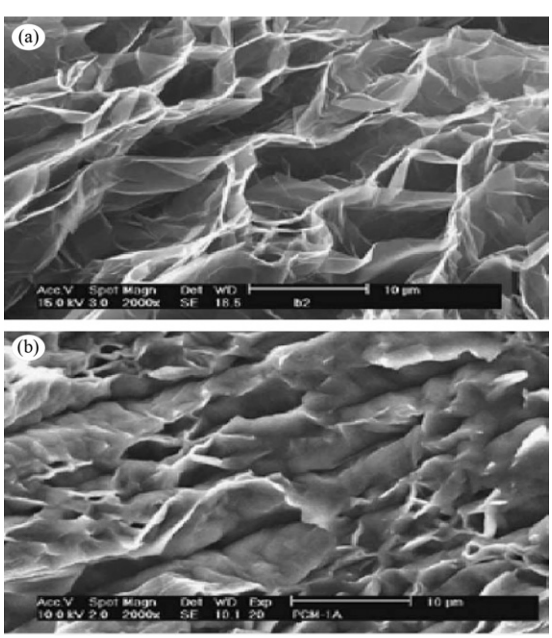


Fig. 6. SEM micrographs of the expanded graphite and the paraffin/expanded graphite composite PCM: (a) expanded graphite; (b) paraffin/expanded graphite composite PCM [49].

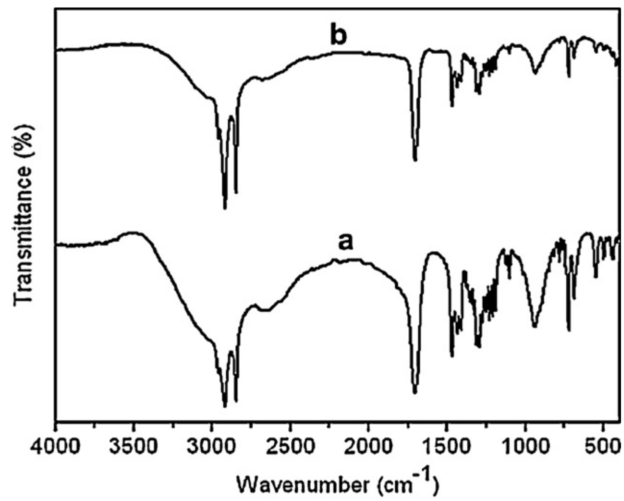


Fig. 7. FTIR spectra of the (a) SA and (b) SA/EG [51].

determine whether there is chemical action between organic PCM and layered material or not.

Detailed information about the interlayer structure and phase state of alkylammonium in silicate interlayer was first obtained using FTIR [53]. Their results revealed that the frequency shift of the CH_2 stretching and scissoring vibrations was a function of interlayer packing density, chain length, and temperature. Fang et al. [51] compared FTIR spectra of stearic acid (SA) and SA/EG. The results are shown in Fig. 7. It is shown that the SA was dispersed in the porous network of the EG. There is no shift in the absorption peaks of the composites when compared with the spectrum of SA. This result indicates that there is no chemical interaction between the functional groups of the SA and the EG. Zhu et al. [54] studied the molecular conformation and mobility of the intercalated surfactant molecules cetyltrimethyl ammonium bromide (CTMAB) using FTIR.

5. Properties of the intercalation composite PCM

The properties of PCM, such as thermal conductivity and flame retardancy, are improved by intercalating into interlayer structure of layered materials. In addition, the effects of intercalating on the phase change temperature and latent heat capacity of organic PCM are also studied.

5.1. Thermal properties

One of the indexes reflecting the heat storage properties is the latent heat capacity. DSC analysis is popular in means available for determining the heat of fusion and the specific heat [55]. The results are listed in Table 3. DSC records the change of heat flux with time. The latent heat capacity is directly proportional with the peak area constituted by the curve and the base line. Fig. 8 shows the DSC thermograms of the intercalation composite PCM [47]. The main peak represents solid–liquid phase change (melting) of paraffin, and the minor peak corresponds to solid–solid phase transition of paraffin. The total latent heats of the composite PCMs are almost equivalent to values calculated by multiplying the latent heat value of pure paraffin (194.6 kJ/kg) with its mass fractions.

T-history method, developed for measuring heat-of-fusion of phase change material (PCM) in sealed tubes, has the advantages of a simple experimental device. Fig. 9 is the schematic diagram of experimental apparatus of T-history method [60].

Fig. 10 is the typical modified T-history curve. Rady and Lázaro [61,62] tested the latent heat capacity using the T-history curve. For this method, Marín et al. [63] proposed a mathematical

Table 3
DSC results of the composite PCMs.

Composite PCMs	Melting point (°C)	Freezing point (°C)	Latent heat (J/g)	References
RT20/montmorillonite	20.8		53.6	[40]
Capric–myristic acid/VMT/2 wt% EG	19.7		26.9	[56]
4% exfoliated graphite nanoplatelets/96% paraffin wax	55.13	51.87	183.5	[57]
Paraffin/expanded graphite	48.93		161.4	[49]
RT20/montmorillonite	20.8		53.6	[40]
70P/22Diatomite/8G	45.4		108.13	[58]
95% paraffin/5% xGnP	50.8		130	[59]

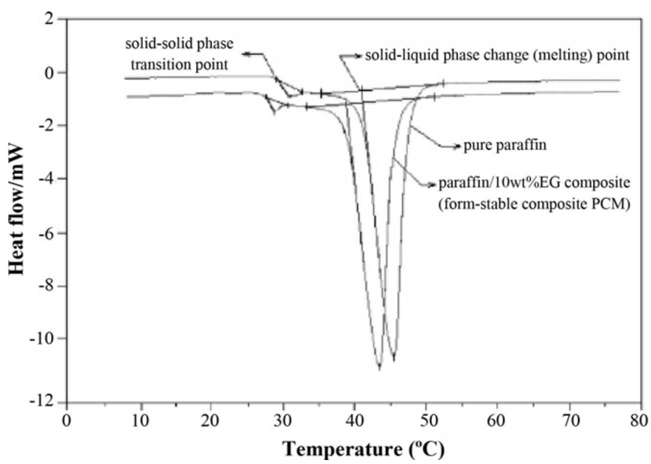


Fig. 8. The DSC thermograms of pure paraffin and paraffin/10 wt% EG composite as form-stable PCM [47].

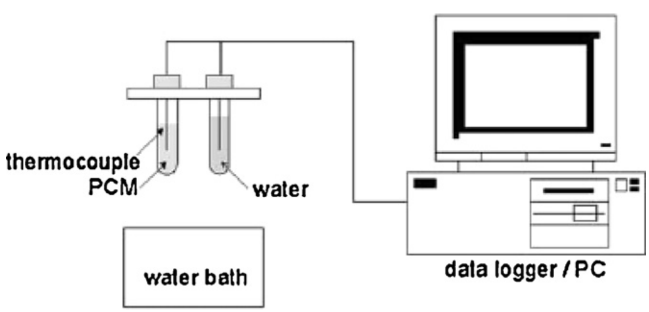


Fig. 9. Schematic diagram of experimental apparatus [60].

improvement in order to obtain the enthalpy as a function of temperature. They also proposed to obtain not only cooling, but also heating curves by using a controller for the ambient temperature. This method has been implemented by the authors in their institutes [64] as well as by other authors [65].

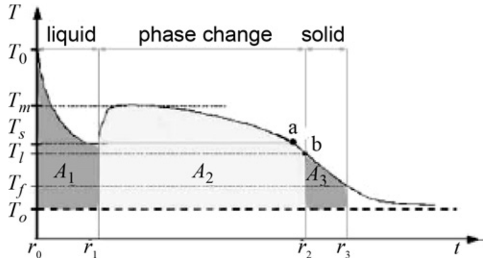


Fig. 10. A typical modified T-history curve [60].

5.2. Thermal conductivity

Majority of PCM has poor conductivity. Therefore, it is necessary to improve thermal properties of PCM in heat storage. It is generally recognized that preparing intercalation composite PCM with graphite is an effective method to improve the thermal conductivity of PCM.

According to the experimental results made by Zhang [66], some additives can improve the thermal conductivity of PCM greatly. When 20% of paraffin is blended into PCM, thermal conductivity of PCM increases to 221% of that of PCM without paraffin. Unfortunately, mechanical strength of PCM decreases sharply after much paraffin is blended in.

Xiao [67] developed a kind of composite material prepared with paraffin, styrene–butadiene–butadiene copolymer and graphite. After solid–liquid phase changing, this kind of material preserves high thermal conductivity and 80% of melting heat of pure paraffin, without liquid phase leak.

Karaipekli [68] did the experiment of improving thermal conductivity of stearic acid with ductile graphite and carbon fiber. The experimental results show that thermal conductivity of stearic acid increases to 266.6% and 206.6%, respectively, when 10% of paraffin or carbon fiber is added, and little latent heat of phase change decreases. Enhancing thermal conductivity with ductile graphite and carbon fiber has the merits (compared with others) as follows: no chemical reactions; dispersing uniformly in PCM; matching well with PCM; lower density than metal; lower weight compared with heat storage system of same volume [69–72].

Sarı and Karaipekli [47] did the experiment to study the composite phase change material prepared with ductile graphite and paraffin. The result shows that the thermal conductivity of pure paraffin and the composite PCM mixed by 2%, 4%, 7% and 10% of paraffin respectively is 0.22, 0.40, 0.52, 0.68 and 0.82 W/m K, respectively. This kind of material has form-stabilized properties without extra encapsulation, and the melting point and latent heat are all suitable.

5.3. Flame retardancy

The flammability of organic PCM has not attracted enough attention and there are very few related literatures presently. Since Fujiwara and Sakamoto reported that clay composite has application potentiality in flame retardancy in 1976 for the first time, many researches work on the flame retardancy of the clay nanocomposite [73]. The results show that adding small quantity of clay can decrease remarkably the peak of heat release rate of materials [74–78]. However, the studies on the flame retardancy of intercalation composite PCM are very few. Cai studied the retardancy of intercalation composite PCM. He indicated that the flame retardancy mechanism of MMT is that coke layer is formed through the combustion of MMT and prevents the further combustion. This flame retardancy mechanism is different from that of flame retardant. Moreover, the addition of MMT does not affect the latent heat capacity of the intercalation composite PCM [79,80].

Sittisart and Farid [80] studied the flame retardancy of intercalation composite PCM composed by paraffin, HDPE, MMT and EG. The results indicated that flame retardancy of the composite PCM (60% paraffin + 40% HDPE) is poor. The flame retardancy of the composite PCM is improved by intercalating paraffin into EG and EG. The flame retardancy of the prepared intercalation composite PCM (60% RT21 + 20% HDPE + 20% EG, 60% RT21 + 15% HDPE + 20% EG + 5% MMT) is good.

6. Conclusions

Intercalation composite PCM is a new kind of composite PCM with some excellent performance. Studies of intercalation composite PCM have been investigated in detail in this paper. They include preparation, structure and properties of the intercalation composite PCM. The following conclusions can be drawn from this paper:

1. PCM can be classified as organic PCM, inorganic PCM and composite PCM by the composition. PCM can be classified as solid–solid, solid–liquid, solid–gas and liquid–gas PCM by the phase. Intercalation composite PCM belongs to solid–liquid composite PCM generally.
2. Intercalation composite PCM mainly includes clay-based and graphite-based intercalation composite PCM. The preparation methods are liquid phase intercalation and melting intercalation. Origination of clay or exfoliation of graphite should be done before being intercalated.
3. The structure of the intercalation composite PCM can be characterized by SEM, XRD and FTIR analysis methods. These methods can determine the layer structure, surface morphology and interaction between organic PCM and layered material.
4. The melting point and the latent heat capacity of the intercalation composite PCM can be measured by DSC and T-history method. The thermal conductivity and flame retardancy of organic PCM are improved by intercalating organic PCM into MMT or EG.

Acknowledgements

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